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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C08G 65/26, C11D 3/37, C08G 65/30</b>		A1	(11) International Publication Number: <b>WO 97/23546</b> (43) International Publication Date: <b>3 July 1997 (03.07.97)</b>
(21) International Application Number: <b>PCT/US96/19094</b> (22) International Filing Date: <b>27 November 1996 (27.11.96)</b>		(81) Designated States: BR, CA, CN, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(30) Priority Data: 08/575,978                    21 December 1995 (21.12.95)            US		Published <i>With international search report.</i>	
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(54) Title: <b>A PROCESS FOR ETHOXYLATING POLYAMINES</b>			
(57) Abstract			
A process for preparing low odor, low color, polyethoxylated polyamines is disclosed. The ethoxylated polyamines described herein are useful for cleaning compositions comprising soil release agents, dispersants, and other nonionic surface active agents.			



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## A PROCESS FOR ETHOXYLATING POLYAMINES

### FIELD OF THE INVENTION

The present invention relates to a process for ethoxylating polyamines, especially polyethyleneimines. The compounds of the present invention comprise low color, low odor ethoxylated amines suitable for use in cleaning compositions.

### BACKGROUND OF THE INVENTION

Ethoxylates of polyamines have wide utility in the field of cleaning compositions, for example they are useful as soil dispersents and chelators among others. When formulating polyamine ethoxylates into laundry detergent compositions, a number of factors determine the suitability of the compounds; among others are viscosity, odor and color.

In the past, higher molecular weight polyamines have been difficult to ethoxylate especially when a narrow degree of average ethoxylation was desired. Longer reaction times and higher process temperatures consistently led to degradation products responsible for the formation of unwanted colors and malodors. In addition, non-reproducible results led to varying levels of final product uniformity which effected the bulk physical properties and thereby hampered uniform processing.

The present invention overcomes many viscosity, color and malodor problems associated with the ethoxylation of polyamines. The reduced off-color of the final product makes the ethoxylated polyamines prepared by the present process, ready for formulation into cleaning compositions comprising other adjunct ingredients and further eliminates the need to use fragrances or colorants to disguise undesirable properties.

While not wishing to be limited by theory, the process according to the present invention reduces the occurrence of side reactions which result in extensive fragmentation of the polyamine backbone or formation of polyethoxylate vinyl ethers. The formation of acetaldehyde, which can undergo further chemical reactions, such as those leading to conjugated chromophores, is likewise greatly reduced. The resulting ethoxylated amines are also uniformly ethoxylated to a greater degree and therefore produce a more consistent product.

Surprisingly, the present process is also adaptable to systems where use of a solvent is desirable to the formulator. Use of solvent may be advantageous in allowing good mixing during ethoxylation particularly when the polyamine and/or

its ethoxylated products have high viscosity in neat form. The use of a solvent in some instances can aid in the further processing of the ethoxylated polyamines, especially when the product is to undergo subsequent chemical transformations. This optional use of a solvent also provides a convenient method of forming certain anhydrous base catalysts, for example, sodium t-butoxide can be produced *in situ* when sodium metal is added to a polyamine dissolved in t-butanol.

Processes for preparing ethoxylated amines are well known in the art, for example, U.S. Patent 4,891,160, Vander Meer, issued January 2, 1990 discloses methods for ethoxylating diamines, polyamines, and polyalkyleneimines comprising an initial step of condensing ethylene oxide with the amine, however, Vander Meer fails to disclose the use of solvents or solvent derived (i.e. alkoxide) base catalysts.

In addition, U.S. Patent 4,551,506, Gosselink, issued November 5, 1985 discloses the use of a base catalyst, however the disclosed amounts of base catalyst used for the U.S. Patent 4,551,506 method is outside the range of the present invention.

It is an object of the present invention to provide a method for ethoxylating polyamino compounds wherein the final product has little or no malodor associated with it. It is a further object of the present invention to provide a method for ethoxylating polyamino compounds wherein color formation is reduced.

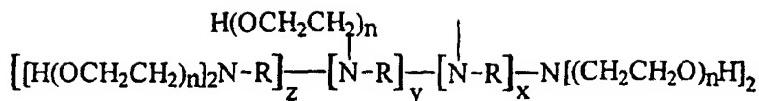
An object of the present invention is to provide a method for ethoxylating polyamino compounds wherein a large choice of anhydrous base catalysts are suitable for use. It is also an object of the present invention to provide a base catalyzed method for ethoxylating polyamines wherein the choice of base catalyst allows the formulator to use suitable solvents and catalyst carriers. It is furthermore an object of the present invention to provide a method for ethoxylating polyamino compounds wherein the final ethoxylated polyamine comprises a narrow range of ethoxylation and that due to lower fragmentation rates, a lower polydispersity ethoxylated product is obtained.

#### BACKGROUND ART

In addition to the above identified U.S. Patents describing the ethoxylation of polyamino compounds, further processes are disclosed in: U.S. Patent 4,622,378, Gosselink, issued November 11, 1986; EP Application 233,010, Collins, et al., published August 19, 1987.

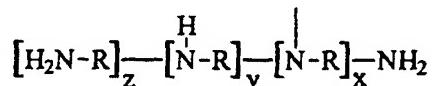
#### SUMMARY OF THE INVENTION

The present invention relates to a method for preparing ethoxylated polyamines of the formula:



wherein R is C<sub>2</sub>-C<sub>22</sub> linear alkylene, C<sub>3</sub>-C<sub>22</sub> branched alkylene, C<sub>8</sub>-C<sub>22</sub> dialkylsubstituted arylene, C<sub>7</sub>-C<sub>22</sub> substituted arylene, and mixtures thereof; n is from about 2 to about 100, x is from 0 to about 300, y is from 0 to about 600, z is from 1 to about 300; comprising the steps of:

- a) reacting a polyamine of the formula:



with ethylene oxide, optionally in the presence of a solvent, until the average value of n is from about 0.75 to about 1.25;

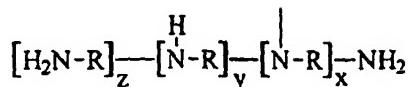
- b) adding from about 2% to about 40% of the total number of N-H equivalents, of a base catalyst, said base catalyst optionally comprising a carrier;
- c) optionally removing the base catalyst carrier by vacuum, heating, or combinations thereof;
- d) further reacting the composition from step (b) or step (c) with ethylene oxide until the average value of n is from 2 to about 100;
- e) neutralizing the base catalyst; and
- f) optionally removing the solvent.

The ethoxylated polyamines of the present invention are preferably polyethylenimines and are generally suitable for use without further purification. The method for preparing the ethoxylated polyamines of the present invention is also suitable for preparing ethoxylated polyamines for use in detergent compositions, for example, soil dispersants, soil release polymers, non-ionic surfactants.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C). All documents cited are, in relevant part, incorporated herein by reference.

#### DETAILED DESCRIPTION OF THE INVENTION

The methods for preparing ethoxylated polyamines according to the present invention involve contacting a polyamine with ethylene oxide, followed by addition of a suitable base catalyst, then re-introduction of ethylene oxide into the reaction matrix until the desired degree of ethoxylation has been achieved. The steps are outlined in more detail as follows.

Step a: A polyamine of the formula

wherein R is C<sub>2</sub>-C<sub>22</sub> linear alkylene, C<sub>3</sub>-C<sub>22</sub> branched alkylene, C<sub>8</sub>-C<sub>22</sub> dialkylsubstituted arylene, C<sub>7</sub>-C<sub>22</sub> substituted arylene, preferably C<sub>2</sub>-C<sub>22</sub> linear alkylene, C<sub>3</sub>-C<sub>22</sub> branched alkylene, more preferably C<sub>2</sub>-C<sub>6</sub> linear alkylene, C<sub>3</sub>-C<sub>6</sub> branched alkylene, still more preferably C<sub>2</sub> linear alkylene (ethylene), and C<sub>3</sub> branched alkylene (1,2-propylene), most preferably R is ethylene, x is from 0 to about 300, y is from 0 to about 600, z is from 1 to about 300; is reacted with ethylene oxide, preferably at a temperature from about 50° C to about 250° C, more preferably from about 40° C to about 180° C, yet more preferably from about 55° C to about 150° C, most preferably from about 80° C to about 120° C, until the average degree of ethoxylation at each reactive original -NH site is from about 0.75 to about 1.25, preferably from about 0.85 to 1.1, more preferably from 0.95 to about 1.

A solvent may be optionally added during step (a). Suitable solvents for use herein are selected from the group consisting of methanol, ethanol, isopropanol, t-butanol, benzene, toluene, xylene, polyethylene glycol having a molecular weight greater than about 100, polypropylene glycol having a molecular weight of from about 100 to about 2000, linear or branched C<sub>8</sub>-C<sub>22</sub> alcohols, alkoxyated linear or branched C<sub>8</sub>-C<sub>22</sub> alcohols, and mixtures thereof

Step b: A base catalyst is added in an amount from about 2% to about 40% of the total number of N-H equivalents present in the polyamine. The base catalyst may optionally comprise a base catalyst carrier. Suitable base catalysts are selected from the group consisting of sodium hydride, potassium hydride, sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide, sodium ethoxide, potassium ethoxide, sodium t-butoxide, potassium t-butoxide, sodium metal, potassium metal, and mixtures thereof, however this list is not meant to be exclusive. Preferred base catalysts are sodium metal and potassium hydroxide, sodium hydroxide, sodium methoxide and sodium t-butoxide.

For the purposes of the present invention the term "base catalyst carrier" is defined as a medium used for the purposes of safely and quantitatively adding the base catalyst. Suitable base catalyst carriers are water, methanol, ethanol, isopropanol, t-butanol, and mixtures thereof, however, this list is not meant to be exclusive. For example, Sodium hydroxide can be suitably introduced into the

reaction process via the carrier water. In addition, sodium hydride and potassium hydride may be introduced into the process of the present invention as slurries in clear, inert mineral oil.

Step c: Any carrier used to introduce the base catalyst is optionally removed at this point. The formulator may use a vacuum, heating, or a combination of heating under a vacuum. Sparging with an inert gas is also a suitable means of removing any carrier. However, it is an optional step to remove any carrier present.

Step d: Ethylene oxide is then further introduced into the reaction vessel whereby the contents of the reaction vessel reacts with ethylene oxide, preferably at a temperature from about 5° C to about 250° C, more preferably from about 40° C to about 180° C, yet more preferably from about 55° C to about 150° C, most preferably from about 80° C to about 130° C, until the average degree of ethoxylation at each reactive site is from about 2 to about 100, preferably from about 2 to about 40, more preferably from about 2 to about 20, even more preferably from about 2 to about 12, most preferably from about 2 to about 7.

Step d: The base catalyst is neutralized with any compatible organic or inorganic acid. For the purposes of the present invention the term "compatible organic or inorganic acid" is defined as any acid that serves the purpose of bringing the reaction mixture to a pH suitable for isolation or further processing of the reaction products. Examples of suitable acids are the C<sub>2</sub>-C<sub>6</sub> aliphatic acids, mineral acids (e.g., HCl, H<sub>2</sub>SO<sub>4</sub>), and others such as methanesulfonic acid, however this list is not limiting. Neutralization may be conducted to any degree that suffices the formulator.

Step e: During this step of the process of the present invention, any solvents or undesired carrier that remains may be removed. This solvent removal may be conducted by using the aid of a vacuum, heat, or combinations thereof. Stripping gases may also be used to remove volatile solvents. In some cases, molecular sieves or zeolites, may be used by the formulator to remove low molecular weight solvents and carriers.

The reactions that comprise the process of the present invention can be carried out in any size reaction vessel. The vessel can be typical laboratory glassware or stainless steel reactors. The reaction can also be carried out in a glass-lined autoclave. The reaction can be conducted on any suitable scale from several hundred milligrams to several thousand kilograms.

Typically the polyamines used for making the ethoxylated polyamines by the process of the present invention, can be used without prior purification, however it is common practice to purge the amines with an inert gas such as nitrogen or argon

prior to heating or contacting with ethylene oxide. The aid of a vacuum for removing any undesirable materials formed during storage of the amines is typical of standard pre-process procedures. The degree to which the polyamine is pre-treated is determined to a large degree by the purity of the starting polyamine.

Once the polyamine to be ethoxylated has been charged to the reaction vessel, a pre-determined amount of ethylene oxide is added. Preferably enough ethylene oxide is introduced to react with each reactive -NH- site so that between 0.75 and 1.25 moles of ethylene oxide have been added per mole of reactive N-H moiety, preferably 0.85 to about 1.05, more preferably from about 0.95 to 1.

The manner in which the ethylene oxide is introduced into the reaction vessel is ultimately left to the formulator, however, certain highly reactive amines may cause an initial exothermic reaction and caution is due particularly on a large scale. Typically, a vacuum is drawn on the head space of the reaction vessel and ethylene oxide is then drawn into the evacuated space through a metered stopcock or pumped in as a liquid and the amount is determined by weight difference or flow meters. Uniformity of reaction is ensured by sufficient mechanical or magnetic stirring.

Once the hydroxyethylation reaction has proceeded to between 0.75 and 1.25 equivalents of ethylene oxide per active -NH- moiety, the base catalyst is added. The term "base catalyst" is defined as any base sufficient to de-protonate the hydroxyl group of a hydroxyethylated amine moiety. The base catalysts can be anhydrous or the base catalysts may be introduced via an aqueous or solvent based carrier. Typical anhydrous base catalysts are sodium metal, sodium hydride or potassium hydride (especially in combination with mineral oil carrier as a dispersion), sodium methoxide, sodium ethoxide, sodium isopropoxide, sodium propoxide, and sodium tert-butoxide, however this list is not meant to be exhaustive. In addition, sodium methoxide or other suitable alkoxide bases may be formed *in situ* by the addition of an alkali metal to a solution of the hydroxyethylated amine dissolved in an appropriate hydroxylic solvent. Sodium t-butoxide solid is also suitable for use and does not necessarily have to be formed *in situ*.

The contents of the reaction vessel is then further reacted with ethylene oxide at a temperature from about 40° C to about 250° C, preferably from about 55° C to about 150° C, more preferably from about 80° C to about 120° C, until the average degree of ethoxylation at each reactive site is from about 2 to about 100.

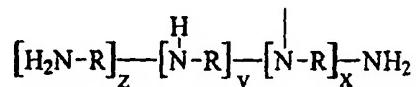
The base catalyst is then neutralized using a suitable acid. Any acid that is compatible with the further formulation and processing of the ethoxylated polyamine is suitable for use in the present process. A preferred acid is methanesulfonic acid.

Next, removal of any solvent present in the reaction mixture is accomplished by any of the standard methods known by those skilled in the art. Typically, for laboratory scale operations under several kilogram, a rotary evaporator is suitable for use in removing the solvent. In addition, thin film evaporators are used for larger scale batches, however in both cases the solvent may be optionally retained.

An advantage of the process of the present invention is that it allows the formulator to prepare a final product that comprises a mixture of more than one laundry product ingredient. Suitable solvents for the process of the present invention include polyethylene glycol having a molecular weight greater than about 100, polypropylene glycol having a molecular weight from about 100 to about 2000, and linear or branched C<sub>8</sub>-C<sub>22</sub> alcohols. The conditions of the present process may be adjusted so that these materials may be co-ethoxylated with the polyamine. Therefore the formulator may produce a mixture of ethoxylate polyamine with other ethoxylated adjunct materials. This step may provide the "intimate mixing" step that is often necessary when formulating water soluble and sparsely water soluble adjunct detergents ingredients.

The Number of Moles of Base Catalyst: Determination of  
the Percentage of the Total -NH Equivalents

In general, the polyamines of the present invention will have a ratio of primary amine: secondary amine:tertiary amine of about 1:2:1, that is the starting polyamines having the general formula



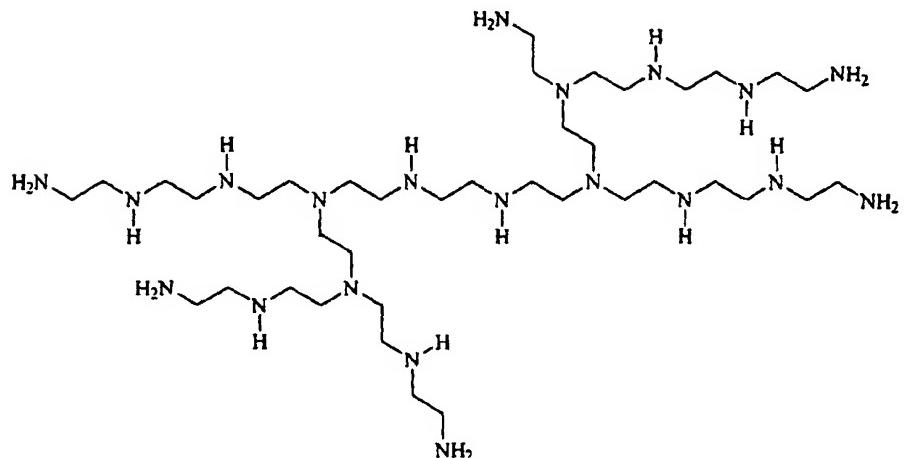
wherein R is the same as defined herein above, and generally have the values of x, y, and z in the ratio of 1:2:1. In the case of ethoxylating polyamines of the general formula



wherein x is from 0 to about 300, y is from 0 to about 600, and w is from 0 to about 22, the ratio of x:y will be approximately 1:2.

The method for calculating "about 2% to about 40% of the total -NH equivalents" is defined as follows. Each -NH function capable of being ethoxylated is considered one equivalent. Primary amine moieties, -NH<sub>2</sub>, comprise two mole equivalents of -NH moieties and secondary amine moieties, -NH-, comprise one

mole equivalent of -NH moieties. For example, the following polyethyleneimine, wherein R is ethylene, having the structure:



has a molecular weight of approximately 934 gm/mole and comprises 6 -NH<sub>2</sub> moieties and 10 -NH- moieties. The total number of -NH equivalents is:

$$\begin{aligned} 2 \times 6 \text{ -NH}_2 &= 12 \\ + 1 \times 10 \text{ -NH-} &= 10 \\ &\quad 22 \text{ -NH equivalents} \end{aligned}$$

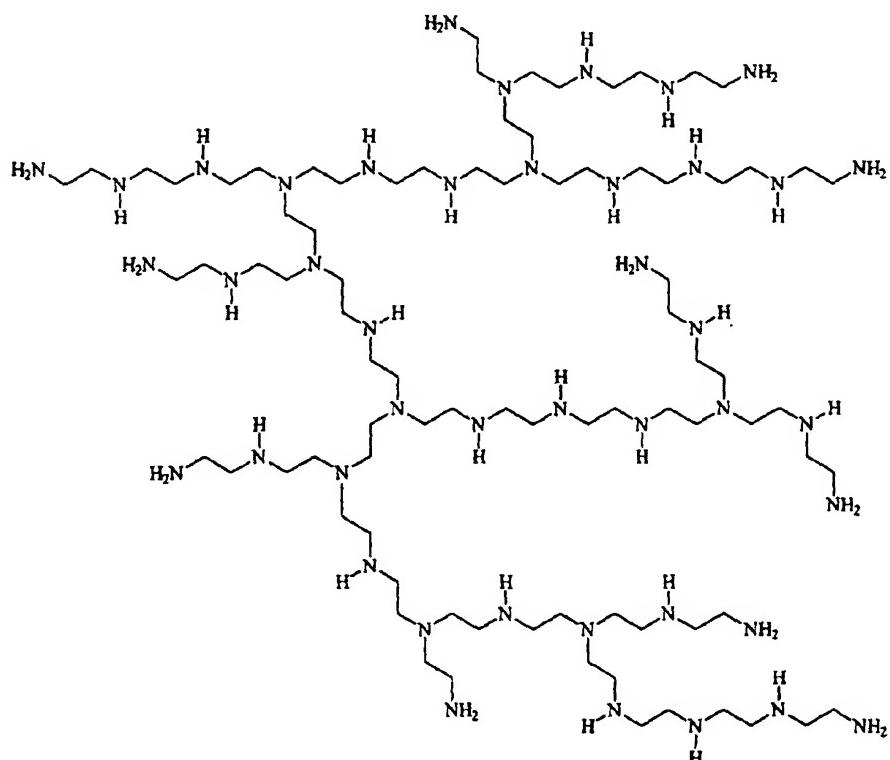
The following table gives an example of the number of grams of catalyst needed in step (b) of the process of the present invention for one mole of the polyethyleneimine shown above having a molecular of 934 gm/mole (PEI 934). The selected levels are 2%, 5%, 25% and 40% of the calculated 22 -NH equivalents present in the polyamine molecule. Calculations are made for four different catalysts.

BASE	2% of -NH moieties (0.44 moles)	5% of -NH moieties (1.1 moles)	25% of -NH moieties (5.5 moles)	40% of -NH moieties (8.8 moles)
NaH MW = 24	10.56 gm	26.4 gm	132.0 gm	211.2 gm
KH MW = 40	17.6 gm	44.0 gm	22.0 gm	352.0 gm
CH <sub>3</sub> ONa MW = 54	23.76 gm	59.4 gm	297.0 gm	475.2 gm
(CH <sub>3</sub> ) <sub>3</sub> COK MW=112	49.28 gm	123.2 gm	616.0 gm	985.6 gm

When the PEI 934, as depicted above, is present in a quantity of one mole, then there are present for the purposes of the present invention, 22 moles of N-H

equivalents. Therefore 22 moles of a base catalyst would be needed to have a level of "100% of the total number of N-H equivalents" of base present. From the table above, 2% of the total N-H equivalents requires 0.44 moles of base and 40% of the total N-H equivalents requires 8.8 moles of base.

A further example, is the following polyethyleneimine with a molecular weight of approximately 1823 gm/mole having the structure:



comprising 11 -NH<sub>2</sub> moieties and 23 -NH- moieties. The total number of -NH equivalents is:

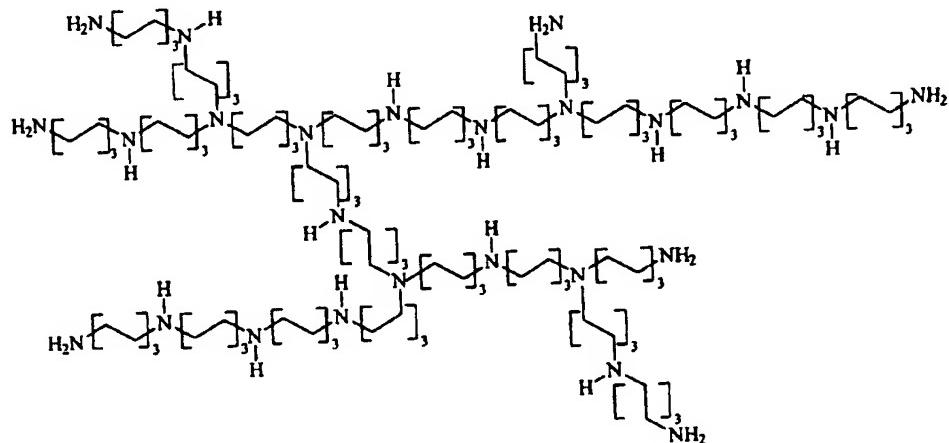
$$\begin{aligned} 2 \times 11 \text{ -NH}_2 &= 22 \\ + 1 \times 23 \text{ -NH-} &= 23 \end{aligned}$$

45 -NH equivalents

The following table gives an example of the number of grams of catalyst needed in step (b) of the process of the present invention for one mole of the polyethyleneimine shown above having a molecular of 1823 gm/mole (PEI 1823). The selected levels are 2%, 5%, 25% and 40% of the calculated 45 -NH equivalents present in the polyamine molecule. Calculations are made for four different catalysts.

BASE	2% of -NH moieties (0.9 moles)	5% of -NH moieties (2.26 moles)	25% of -NH moieties (11.3 moles)	40% of -NH moieties (18.1 moles)
NaH MW = 24	21.65 gm	54.3 gm	271.3 gm	434.4 gm
KH MW = 40	36.08 gm	90.3 gm	451.3 gm	722.4 gm
CH <sub>3</sub> ONa MW = 54	48.71 gm	121.8 gm	608.9 gm	974.4 gm
(CH <sub>3</sub> ) <sub>3</sub> COK MW=112	101.02 gm	253.0 gm	1265.0 gm	2024.0 gm

A further example, is the following polyhexyleneamine with a molecular weight of approximately 2393 gm/mole having the structure:



comprising 7 -NH<sub>2</sub> moieties and 13 -NH- moieties. The total number of -NH equivalents is:

$$\begin{aligned}
 2 \times 7 \text{ -NH}_2 &= 14 \\
 + 1 \times 13 \text{ -NH-} &= 13 \\
 \hline
 27 \text{ -NH equivalents}
 \end{aligned}$$

The following table gives an example of the number of grams of catalyst needed in step (b) of the process of the present invention for one mole of the polyhexyleneamine shown above having a molecular weight of 2393 gm/mole (PEA 2393). The selected levels are 2%, 5%, 25% and 40% of the calculated 27 -NH equivalents present in the polyamine molecule. Calculations are made for four different catalysts.

BASE	2% of -NH moieties (0.54 moles)	5% of -NH moieties (1.35 moles)	25% of -NH moieties (6.75 moles)	40% of -NH moieties (10.8 moles)
NaH MW = 24	13.0 gm	32.4 gm	162.0 gm	259.2 gm
KH MW = 40	21.6 gm	54.0 gm	270.0 gm	432.0 gm
CH <sub>3</sub> ONa MW = 54	29.2 gm	72.9 gm	364.5 gm	583.2 gm
(CH <sub>3</sub> ) <sub>3</sub> COK MW=112	60.5 gm	151.2 gm	756.0 gm	1209.6 gm

The following is an example in which polyethoxylated polyamines are prepared according to the method of present invention.

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (Nippon Shokubai, Epomin SP-018 having a listed average molecular weight of 1800 equating to about 0.417 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the

autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

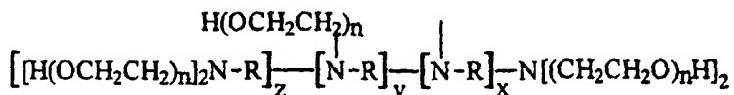
The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

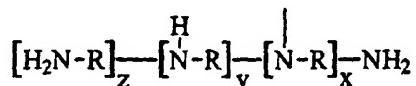
WHAT IS CLAIMED IS:

1. A method for preparing ethoxylated polyamines of the formula:



wherein R is C<sub>2</sub>-C<sub>22</sub> linear alkylene, C<sub>3</sub>-C<sub>22</sub> branched alkylene, C<sub>8</sub>-C<sub>22</sub> dialkylsubstituted arylene, C<sub>7</sub>-C<sub>22</sub> substituted arylene, and mixtures thereof; n is from 2 to 100, x is from 0 to 300, y is from 0 to 600, z is from 1 to 300; comprising the steps of:

- a) reacting a polyamine of the formula:



the with ethylene oxide, optionally in the presence of a solvent, until average value of n is from 0.75 to 1.25, preferably from 0.85 to 1.1, more preferably from 0.95 to 1;

- b) adding from 2% to 40% of the total number of N-H equivalents, a base catalyst, said base catalyst optionally comprising a carrier;
- c) optionally removing the base catalyst carrier by vacuum, heating, or combinations thereof;
- d) further reacting the composition from step (b) or step (c) with ethylene oxide until the average value of n is from 2 to 100, preferably from 2 to 40, more preferably from 2 to 20, and most preferably from 2 to 7;
- e) neutralizing the base catalyst; and
- f) optionally removing the solvent.

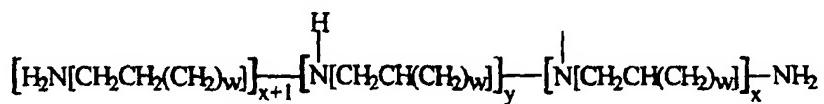
2. A method according to Claim 1 wherein R is C<sub>2</sub>-C<sub>22</sub> linear alkylene, C<sub>3</sub>-C<sub>22</sub> branched alkylene, and mixtures thereof; preferably C<sub>2</sub>-C<sub>6</sub> linear alkylene, C<sub>3</sub>-C<sub>6</sub> branched alkylene, and mixtures thereof; more preferably C<sub>2</sub> linear alkylene, C<sub>3</sub> branched alkylene, and mixtures thereof; and most preferably C<sub>2</sub> linear alkylene.

3. A method according to either of Claims 1 or 2 wherein step (a) is conducted at a temperature of from 5° C to 250° C, preferably from 40° C to 180°

C, more preferably from 55° C to 150° C, and most preferably from 80° C to 120° C.

4. A method according to any of Claims 1 - 3 wherein step (d) is conducted at a temperature of from 5° C to 250° C, preferably from 40° C to 180° C, more preferably from 55° C to 150° C, and most preferably from 80° C to 120° C.

5. A method for ethoxylating a polyamino compound having the formula:



wherein w is from 0 to 20, preferably from 0 to 12, more preferably from 0 to 6, most preferably 0 or 1, x is from 0 to 300 and y is from 0 to 600; comprising the steps of:

- a) reacting said polyamino compound with ethylene oxide at a temperature of from 5° C to 250° C, preferably from 40° C to 180° C, more preferably, from 55° C to 150° C, most preferably from 80° C to 120° C, optionally in the presence of a solvent, until the average degree of ethoxylation is from 0.75 to 1.25, preferably from 0.85 to 1.1, more preferably from 0.95 to 1;
- b) adding from 2% to 40% of the total number of N-H equivalents, a base catalyst, said base catalyst optionally comprising a carrier;
- c) optionally removing the base catalyst carrier when a base catalyst carrier is present by means of a vacuum, heating, or combinations thereof;
- d) reacting additional ethylene oxide with the polyamino compound of step (b) or step (c) until said polyamino compound has an average degree of ethoxylation of from 2 to 50, preferably from 2 to 15, more preferably from 5 to 10, at a temperature of from 5° C to 250° C, preferably from 40° C to 180° C, more preferably from 55° C to 150° C, and most preferably from 80° C to 120° C;
- e) optionally neutralizing the base catalyst; and
- f) optionally removing the solvent.

6. A method according to any of Claims 1 - 5 wherein the base catalyst is selected from the group consisting of sodium hydride, potassium hydride, sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide, sodium ethoxide, potassium ethoxide, sodium t-butoxide, potassium t-butoxide, sodium metal, potassium metal, and mixtures thereof.

7. A method according to any of Claims 1 - 6 wherein the base catalyst carrier is selected from the group consisting of water, methanol, ethanol, isopropanol, t-butanol, and mixtures thereof.

8. A method according to any of Claims 1 - 7 wherein the solvent is methanol, ethanol, isopropanol, t-butanol, benzene, toluene, xylene, polyethylene glycol having a molecular weight greater than 100, polypropylene glycol having a molecular weight of from 100 to 2000, linear or branched C<sub>8</sub>-C<sub>22</sub> alcohols, alkoxylated linear or branched C<sub>8</sub>-C<sub>22</sub> alcohols, and mixtures thereof.

## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/US 96/19094

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08G65/26 C11D3/37 C08G65/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08G C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 32272 A (PROCTER & GAMBLE) 30 November 1995 see example 2 see page 7, line 26 - line 37 ---	1-8
A	EP 0 112 593 A (PROCTER & GAMBLE) 4 July 1984 cited in the application see page 14, line 1 - line 15 ---	1-8
A	EP 0 539 819 A (BASF AG) 5 May 1993 see example 1 see page 5, line 44 - page 6, line 8 ---	1-8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*'A' document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

Date of mailing of the international search report

12.03.97

27 February 1997

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## INTERNATIONAL SEARCH REPORT

In' tional Application No PCT/US 96/19094
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 361 (C-459), 25 November 1987 & JP 62 131020 A (NIPPON OIL & FATS CO LTD), 13 June 1987, see abstract ----	1-8
A	US 3 251 778 A (DICKSON W.J. ET AL) 17 May 1966 see column 10, line 50 - line 62 -----	1-8

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

Int'l Application No
PCT/US 96/19094

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9532272 A	30-11-95	AU 2387095 A CA 2189749 A US 5565145 A	18-12-95 30-11-95 15-10-96
EP 0112593 A	04-07-84	US 4597898 A AU 575034 B AU 2280283 A CA 1220395 A EG 17032 A GB 2133415 A,B GB 2175597 A,B GB 2180249 A,B HK 58390 A HK 58790 A HK 74590 A JP 1773204 C JP 4054719 B JP 59166598 A US 4891160 A CA 1213286 A	01-07-86 21-07-88 28-06-84 14-04-87 30-10-93 25-07-84 03-12-86 25-03-87 10-08-90 10-08-90 28-09-90 14-07-93 01-09-92 19-09-84 02-01-90 28-10-86
EP 0539819 A	05-05-93	DE 4135588 A CA 2080516 A JP 5214091 A US 5476969 A	06-05-93 30-04-93 24-08-93 19-12-95
US 3251778 A	17-05-66	NONE	

